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(54) **Phosphate flame retardant polymer**

(57) A flame retardant moldable thermoplastic resin composition consisting of a thermoplastic resin and a flame retardant consisting of a combination of a low molecular weight phosphate having a molecular weight of about 500 to about 2000 and a high molecular weight

phosphate having a molecular weight of about 2300 to about 11,000 and to articles molded therewith. The composition has a high heat deflection temperature, good impact resistance, excellent flame retardancy and good flow for easier processing.

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Description

The present invention relates to flame retarded polymer composition for molding applications which polymer composition comprises in admixture a thermoplastic molding resin and a particular phosphate flame retardant. The phosphate flame retardant comprises a combination or mixture of two phosphates, namely a low molecular weight and a high molecular weight phosphate and to articles molded with the composition of this invention.

The prior art has disclosed the use of phosphates as flame retardants for polymers or thermoplastic molding resins particularly such monophosphates as triphenyl phosphate, tricresyl phosphate, diphenylcresyl phosphate and the like. Such monophosphate esters tend to migrate to the surface when the thermoplastic composition is molded such as injection molding causing so called "juicing." Juicing is where the additive migrates to the surface of the molded article during molding. Also in order to obtain good flame retardancy, often other flame retardants need to be employed with the monophosphate esters, particularly halogen containing flame retardants. Halogen flame retardants are undesirable because of the environment concerns and the pitting of the mold surface. On the other hand, if high concentrations of the particular phosphate esters are employed a decrease in heat resistance and impact resistance can result.

Gosen et al U.S. Patent 5,204,394 discloses a composition of an aromatic polycarbonate, a styrene containing copolymer such as acrylonitrile-butadiene-styrene (ABS) and oligomeric phosphate flame retardants. The patent further discloses that the oligomeric phosphate employed therein may be a blend of several different oligomers (column 4 lines 46-66).

However, no prior art example has been uncovered that discloses the use of high molecular weight phosphates as flame retardant, i.e. the high molecular weights of the magnitude employed herein, or the combination of a low molecular weight phosphate and a high molecular weight phosphate as employed in the instant invention.

Therefore, the object of the present invention is to provide a thermoplastic molding composition having good flame retardant properties without the use of halogenated flame retardant.

A further object of the present invention is to provide a flame retardant composition having good heat deflection temperature and impact resistance.

Another object of the present invention is to provide a flame retardant molded thermoplastic article prepared from the composition of this invention and having good mechanical properties of heat deflection and impact resistance.

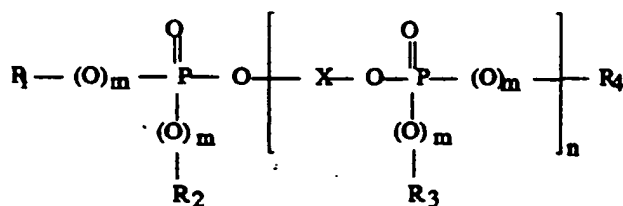
These and other objects of this invention will become apparent from the following description of this invention.

SUMMARY OF THE INVENTION

This invention is directed to a thermoplastic resin molding composition having excellent flame retardant properties using a non halogenated flame retardant while maintaining good mechanical properties of heat deflection temperature, impact resistance and flow. Specifically the flame retardant employed herein is a combination of a low molecular weight phosphate and a high molecular weight phosphate. The low molecular weight phosphate has a molecular weight of at least about 500 and preferably about 500 to about 2000. The high molecular weight phosphate has a molecular weight of at least about 2300 and preferable about 2300 to about 11,000.

DETAILED DESCRIPTION OF THE INVENTION

As stated previously, the invention is directed to a flame retardant thermoplastic molding composition and to articles molded therefrom. The flame retardant thermoplastic molding composition comprises in admixture a thermoplastic molding resin and a flame retardant additive comprising in combination a low molecular weight and a high molecular weight phosphate. The phosphates employed herein are preferably represented by the following formula:



wherein R_1 , R_2 , R_3 and R_4 are independently selected from the group consisting of an aryl or an alkaryl group, X is an arylene group, m is an integer of from 0 or 1. In the case of the low molecular weight phosphate, the phosphate is an oligomeric phosphate wherein n is an integer of from 1 to 5. The low molecular weight phosphate of this invention with

or without this above formula has a molecular weight of at least about 500 and preferable about 500 to about 2000 wherein n is 1 to 5. The high molecular weight phosphate of this invention with or without this above formula has a molecular weight of at least about 2300 and preferably about 2300 to about 11,000 wherein n is an integer of from about 6 to 35. More preferably, the high molecular weight phosphate of this invention has a molecular weight of at least about 5000 and most preferably at least about 7500. It is important that the molecular weight of the low molecular weight phosphate does not overlap the molecular weight of the high molecular weight phosphate.

In the above formula, the aryl groups may be aryl or an alkyl substituted aryl group thus alkaryl groups. Preferable the aryl groups are independently selected from cresyl, phenyl, xylenyl, propylphenyl and butylphenyl groups. The arylene group is derived from a dihydric compound and is preferable resorcinol, hydroquinone and bisphenol-A. More particularly the aryl group (R_1 , R_2 , R_3 and R_4) is phenyl and the more particular arylene group is bisphenol-A. In the case of the low molecular weight phosphates, the more preferred low molecular weight phosphate is bisphenol-A tetraphenyl diphosphate wherein n is 1, m is 1, X is bisphenol-A and the R's are phenyl with this more preferred low molecular weight phosphate having a molecular weight of about 693.

In the case of the high molecular weight phosphate, the most preferred is bisphenol-A phenyl polyphosphate having a molecular weight of about 10,056. In this most preferred high molecular weight phosphate of the above formula, the R's are phenyl groups, X is bisphenol-A, m is 1 and n is about 32.

In the practice of the invention, the thermoplastic resin employed herein can be any of the thermoplastic molding resins that can be molded by injection molding, compression molding, transfer molding, extrusion blow molding or profile extrusion. The preferred thermoplastic molding resins are aromatic polycarbonates, high impact polystyrenes, styrene containing copolymers and styrene containing graft copolymers such as acrylonitrile-butadiene-styrene (ABS) resins, polyphenylene ether resins, polyalkylene terephthalate resins such as polybutylene terephthalate, polyethylene terephthalate, and polypropylene terephthalate resins, polyether imide resins, polyether imide ester resins, polyamide resins, polyphenylsulfide resins, polyphenyl sulfones, polyimide resins and mixtures thereof. The most preferred resins are aromatic polycarbonates, blends of aromatic polycarbonates and ABS, blends of polyphenylene ethers and high impact polystyrenes, and polyether imides.

The amount of phosphate employed can be that amount of phosphate which renders the thermoplastic molding resin composition flame retardant while maintaining good properties of heat deflection temperature, impact resistance and flow. Preferable the composition of the invention contains about 3 to about 25 weight percent of the phosphate flame retardant based on the total weight of thermoplastic resin and phosphate flame retardant and preferably about 5 to about 20 weight percent thereof.

The flame retardant of this invention is a combination of a low molecular weight and a high molecular weight phosphate. The flame retardant consists essentially of about 10 to about 90 weight % of the low molecular weight phosphate and correspondingly 90 to about 10 weight % of the high molecular weight phosphate based on the weight of the flame retardant. Preferable the combination of phosphates consists essentially of about 40 to about 70 weight % of the low molecular weight phosphate and correspondingly about 60 to about 30 weight % of the high molecular weight phosphate. In addition, other additives may be employed with the composition of this invention such as other flame retardant enhancing additives, reinforcing additives such as glass fibers, other mineral additives such as mica, talc, oxides, including plasticizers, light and heat stabilizer, processing aides, impact modifiers, mold release agents, etc.

The compositions of this invention produce molded articles having a combination of excellent properties, depending on the thermoplastic resin employed and the application for the molded article. Preferably, molded articles from the composition of this invention have a matched Izod of at least about 5.0 ft.-lbs/in., as determined in accordance with ASTM D 256, a heat deflection temperature under load of at least about 200°F as determined in accordance with ASTM D 648, a flow of at least about 18" by the spiral flow measurement of a 1/8" thick channel and a flammability rating of at least V1 as determined in accordance with Underwriters Laboratory Bulletin UL 94. In the case of an ABS injection molding resin employing the flame retardant of this invention, an injection molded article may preferably have a notched Izod of at least about 7.0 ft.-lbs/in., a heat deflection temperature under load of at least about 200°F, a flow of at least about 25.0" and a UL 94 rating of at least V1. In the case of a polyphenylene ether resin system employing the flame retardant of this invention, an injection molded article may preferably have a heat deflection temperature of at least about 200°F, a flow of at least about 15" and a UL 94 rating of at least V1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following Examples are provided to illustrate various embodiments of this invention. The Examples are for the purpose of illustration only, and should not be regarded as limiting the invention to any of the specific materials or conditions described therein.

EXAMPLE 1

The materials employed in this Example as components parts were as follows:

- 5 PC- an aromatic polycarbonate derived from bisphenol-A and a carbonyl chloride (phosgene) having a weight average molecular weight of about 22,000 and an intrinsic viscosity (I.V.) of about 0.40 dl/g as measured in methylene chloride at 25°C
- HRG- a high rubber graft copolymer prepared by grafting a styrene-acrylonitrile onto a butadiene rubber in a 50/50 ratio
- 10 Phosphate 1 - a mixture of several oligomeric diphosphates based on resorcinol
- Phosphate 2 - Bisphenol-A tetraphenyl diphosphate having a molecular weight of about 693.
- Phosphate 3 - Bisphenol-A phenyl polyphosphate having a molecular weight of about 10,056.
- PTFE - polytetrafluoroethylene

15 The components of the formulations as reported in Table 1 were compounded in a 30mm Werner Pfleider twin screw extruder at melt temperatures of about 550 - 560°F and extruded. The extrudate was pelletized and the pellets were then dried at about 190°F for about three (3) hours. The pellets were then molded into standard test specimens in accordance with the ASTM test procedure employed for determining the particular properties which are reported in Table 1 below. Impact resistance was determined by the Notched Izod impact test procedure ASTM D256 on molded

20 specimens having a thickness of about 1/8". Heat deflection temperatures (HDT) under load (264 psi) were measured on molded 1/4" test bars in accordance with ASTM test procedure D648. Spiral flow measurements were performed in a 1/8" thick channel at a melt temperature of about 480°F and a mold temperature of about 150°F. The higher the length of the flow, the better is the flow of the specimen and easier to process. Flammability was determined on 1/16" thick test specimens in accordance with Underwriters Laboratory Bulletin UL94 flammability rating V0, V1 and V2.

25 The results of the test are regarded in Table 1 below:

Table 1

Blend	1	2	3	4
HRG	81.05	80.05	80.05	80.05
Phosphate 1				11
Phosphate 2	10		6	
Phosphate 3		11	5	
PTFE	.2	.2	.2	.2
Additives	.95	.95	.95	.95
PROPERTIES				
Notched Izod (ft-lb/in)	9.0	7.1	8.6	2.3
HDT (°F)	204	236	214	188
Flow Channell (")	28	25.5	29.75	32.5
UL 94 (1/16")	V0	V2	V0	V0
Additives - stabilizer package of a hindered phenol, a phosphite and a lubricant				

EXAMPLE 2

50 Example 1 was repeated except that the formulations employed herein are as reported in Table 2 below. The polyphenylene ether employed had an I.V. of about 0.46 dl/g and was produced by General Electric Company. The high impact polystyrene (HPS) was produced by GE-Huntsman Co., Selkirk, New York, and had a weight average molecular weight of about 200,000 and a rubber content of about 10½ weight % based on the weight of the high impact

55 polystyrene. The properties obtained were determined employing the same test procedures employed in Example 1. The results obtained are set forth in Table 2 below.

Table 2

Blend	1	2
Polyphenylene ether	50.5	50.5
High impact PS (HPS)	28	28
Phosphate 1	16.7	10.7
Phosphate 3	0	6.0
Polyethylene	1.25	1.25
Additives	1.0	1.0
Impact modifier	2.55	2.55
PROPERTIES		
HDT (°F)	193	228
Flow Channel (")	20.5	19.75
UL 94	V0	V0
PS - Polystyrene Impact modifier - a styrene-butadiene block copolymer produced by Shell Chemical Co., Kraton G1650 Additives - a stabilizer package of a phosphite, an oxide and a sulfide Polyethylene - a mold release agent		

As shown from the Examples, the use of a low molecular weight and a high molecular weight phosphate produced results of good impact resistance, high heat deflection temperature under load, good flow for easy processing and excellent flame resistance. This is shown in Table 1 blend 3 in comparison to the other blends. Please note blend 1 which employed a low molecular weight bisphenol-A tetraphenyl diphosphate (oligomeric diphosphate); blend 2 which employed a high molecular weight bisphenol-A polyphosphate; and blend 4 which employed a mixture of oligomeric diphosphates. The unexpected results showed that the composition of this invention (blend 3) had good overall properties compared to the comparative blends 1, 2 and 4. In Table 2, equivalent results were obtained when employing a polyphenylene ether composition. Significantly better heat deflection temperature under load (264 psi) was obtained with the composition of this invention namely blend 2 of Table 2. Also flame retardant migration (juicing) was noticeably lacking from the composition of this invention.

In addition to the polymers employed in these Examples, the other polymers disclosed herein will produce equivalent results to those obtained with the polymers of Example 1 and 2.

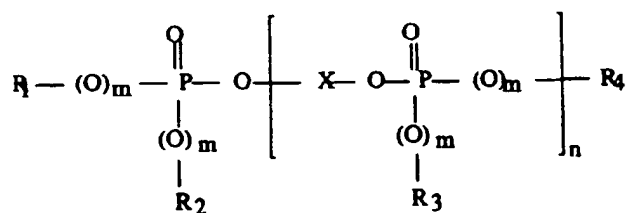
While variations of this invention will be suggested to those skilled in the art, in view of the above disclosure, any such variations are intended to be within the scope of the claims appended hereto.

Claims

1. A moldable flame retardant thermoplastic resin composition comprising in admixture a moldable thermoplastic resin and a sufficient amount of a flame retardant to render the composition flame retardant which flame retardant consists essentially of, in combination, a low molecular phosphate having a molecular weight of at least about 500 and a high molecular weight phosphate having a molecular weight of at least about 2300, providing that the molecular weights do not overlap each other.
2. The composition of claim 1 wherein the low molecular weight phosphate has a molecular weight of about 500 to about 2000.
3. The composition of claim 1 wherein the high molecular weight phosphate has a molecular weight of about 2300 to about 11,000.
4. The composition of claim 1 wherein the flame retardant consists essentially of about 10 to 90 weight % of the low molecular weight phosphate and, correspondingly, about 90 to 10 weight % of the high molecular weight phosphate

based on the total weight of the phosphate flame retardant.

5. The compositions of claim 1 wherein the thermoplastic resin is selected from the group consisting of aromatic polycarbonates, polyphenylene ethers, polyalkylene terephthates, polyetherimides, polyetherimide esters, polyamides, styrene containing polymers and blends thereof.
6. The composition of claim 5 wherein the thermoplastic resin is an admixture of an aromatic polycarbonate and a styrene containing polymer.
7. The composition of claim 5 wherein the thermoplastic resin is an admixture of a polyphenylene ether resin and a high impact polystyrene.
8. The composition of claim 1 consisting essentially of about 75 to about 97 weight % of the thermoplastic resin and, correspondingly, about 25 to about 3 weight % of the flame retardant.
9. The composition of claim 1 wherein the low molecular weight phosphate is of the following formula:



Wherein R1, R2, R3 and R4 are independently selected from the group consisting of an aryl or an alkylaryl group; X is an arylene group; m is an integer of from 0 and 1; n is an integer of from 1 to 5; and P is phosphorous.

10. The composition of claim 9 wherein the high molecular weight phosphate is of the same formula and n is an integer of from 6 to 35.



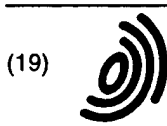
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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 3937

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A,D	EP-A-0 363 608 (GENERAL ELECTRIC) * page 5, line 24 - line 28 * * page 4, line 11 - line 22 * * claims 1,7,13,14; tables C,D * ---	1-3,5,6, 8,9	C08K5/523 C08L85/02 C08L101/00
A	EP-A-0 103 231 (BAYER) * page 16, line 10 - line 15 * * page 18, line 19 * * page 26, line 5 - line 8 * * claims 1,3; examples * ---	1-3,5,6, 8	
A	EP-A-0 103 230 (BAYER) * page 17, line 8 - line 18 * * claims 1,3; examples; tables * ---	1-3,5,6	
A X	WO-A-93 04119 (GENERAL ELECTRIC) * page 14, paragraph 3 * * claims 1,21 * ---	1-5,8-10 1,5,9,10	
P,X	DATABASE WPI Section Ch, Week 9621 Derwent Publications Ltd., London, GB; Class A13, AN 96-205657 XP002013028 & JP-A-08 073 654 (ASAHI KASEI KOGYO KK) , 19 March 1996 * abstract * ---	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08K C08L
A	DATABASE WPI Section Ch, Week 8305 Derwent Publications Ltd., London, GB; Class A25, AN 83-11203K XP002013029 & JP-A-57 207 641 (ADEKA-ARGUS CHEM KK) , 20 December 1982 * abstract * -----	1,5,7,9	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 September 1996	Examiner Engel, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

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(22) Date of filing: **31.05.1996**

(54) **Phosphate flame retardant polymer**

Phosphatflamhemmer-Polymer

Polymère ignifuge phosphaté

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EP-A- 0 103 230 EP-A- 0 103 231
EP-A- 0 363 608 WO-A-93/04119

- **DATABASE WPI Section Ch, Week 9621 Derwent Publications Ltd., London, GB; Class A13, AN 96-205657 XP002013028 & JP-A-08 073 654 (ASAHI KASEI KOGYO KK) , 19 March 1996**
- **DATABASE WPI Section Ch, Week 8305 Derwent Publications Ltd., London, GB; Class A25, AN 83-11203K XP002013029 & JP-A-57 207 641 (ADEKA-ARGUS CHEM KK) , 20 December 1982**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

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Description

[0001] The present invention relates to flame retarded polymer composition for molding applications which polymer composition comprises in admixture a thermoplastic molding resin and a particular phosphate flame retardant. The phosphate flame retardant comprises a combination or mixture of two phosphates, namely a low molecular weight and a high molecular weight phosphate and to articles molded with the composition of this invention.

[0002] The prior art has disclosed the use of phosphates as flame retardants for polymers or thermoplastic molding resins particularly such monophosphates as triphenyl phosphate, tricresyl phosphate, diphenylcresyl phosphate and the like. Such monophosphate esters tend to migrate to the surface when the thermoplastic composition is molded such as injection molding causing so called "juicing." Juicing is where the additive migrates to the surface of the molded article during molding. Also in order to obtain good flame retardancy, often other flame retardants need to be employed with the monophosphate esters, particularly halogen containing flame retardants. Halogen flame retardants are undesirable because of the environment concerns and the pitting of the mold surface. On the other hand, if high concentrations of the particular phosphate esters are employed a decrease in heat resistance and impact resistance can result.

[0003] Gosen et al U.S. Patent 5,204,394 discloses a composition of an aromatic polycarbonate, a styrene containing copolymer such as acrylonitrile-butadiene-styrene (ABS) and oligomeric phosphate flame retardants. The patent further discloses that the oligomeric phosphate employed therein may be a blend of several different oligomers (column 4 lines 46-66).

[0004] However, no prior art example has been uncovered that discloses the use of high molecular weight phosphates as flame retardant, i.e. the high molecular weights of the magnitude employed herein, or the combination of a low molecular weight phosphate and a high molecular weight phosphate as employed in the instant invention.

[0005] Therefore, the object of the present invention is to provide a thermoplastic molding composition having good flame retardant properties without the use of halogenated flame retardant.

[0006] A further object of the present invention is to provide a flame retardant composition having good heat deflection temperature and impact resistance.

[0007] Another object of the present invention is to provide a flame retardant molded thermoplastic article prepared from the composition of this invention and having good mechanical properties of heat deflection and impact resistance.

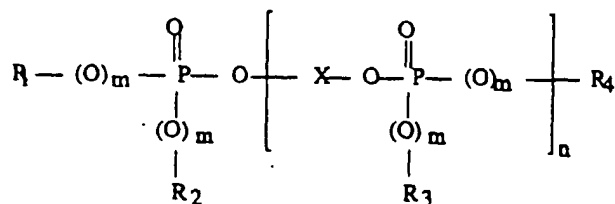
[0008] These and other objects of this invention will become apparent from the following description of this invention.

SUMMARY OF THE INVENTION

[0009] This invention is directed to a thermoplastic resin molding composition having excellent flame retardant properties using a non halogenated flame retardant while maintaining good mechanical properties of heat deflection temperature, impact resistance and flow. Specifically the flame retardant employed herein is a combination of a low molecular weight phosphate and a high molecular weight phosphate. The low molecular weight phosphate has a molecular weight of at least about 500 and preferably 500 to 2000. The high molecular weight phosphate has a molecular weight of at least about 2300 and preferably 2300 to 11,000.

DETAILED DESCRIPTION OF THE INVENTION

[0010] As stated previously, the invention is directed to a flame retardant thermoplastic molding composition and to articles molded therefrom. The flame retardant thermoplastic molding composition comprises in admixture a thermoplastic molding resin and a flame retardant additive comprising in combination a low molecular weight and a high molecular weight phosphate. The phosphates employed herein are represented by the following formula:



wherein R_1 , R_2 , R_3 and R_4 are independently selected from the group consisting of an aryl or an alkaryl group, X is derived from bisphenol-A, m is 0 or 1. In the case of the low molecular weight phosphate, the phosphate is an oligomeric phosphate wherein n is an integer of from 1 to 5. The low molecular weight phosphate has a molecular weight of at

least about 500 and preferably from 500 to 2000 wherein n is 1 to 5. The high molecular weight phosphate of this invention has a molecular weight of at least 2300 and preferably 2300 to 11,000 wherein n is an integer of from 6 to 35. More preferably, the high molecular weight phosphate of this invention has a molecular weight of at least about 5000 and most preferably at least about 7500. It is important that the molecular weight of the low molecular weight phosphate does not overlap the molecular weight of the high molecular weight phosphate.

[0011] In the above formula, the aryl groups may be aryl or an alkyl substituted aryl group thus alkaryl groups. Preferable the aryl groups are independently selected from cresyl, phenyl, xylenyl, propylphenyl and butylphenyl groups. More particularly the aryl group (R_1 , R_2 , R_3 and R_4) is phenyl. In the case of the low molecular weight phosphates, the more preferred low molecular weight phosphate is bisphenol-A tetraphenyl diphosphate wherein n is 1, m is 1, X is bisphenol-A and the R's are phenyl with this more preferred low molecular weight phosphate having a molecular weight of about 693.

[0012] In the case of the high molecular weight phosphate, the most preferred is bisphenol-A phenyl polyphosphate having a molecular weight of about 10,056. In this most preferred high molecular weight phosphate of the above formula, the R's are phenyl groups, X is bisphenol-A, m is 1 and n is about 32.

[0013] In the practice of the invention, the thermoplastic resin employed herein can be any of the thermoplastic molding resins that can be molded by injection molding, compression molding, transfer molding, extrusion blow molding or profile extrusion. The preferred thermoplastic molding resins are aromatic polycarbonates, high impact polystyrenes, styrene containing copolymers and styrene containing graft copolymers such as acrylonitrile-butadiene-styrene (ABS) resins, polyphenylene ether resins, polyalkylene terephthalate resins such as polybutylene terephthalate, polyethylene terephthalate, and polypropylene terephthalate resins, polyether imide resins, polyether imide ester resins, polyamide resins, polyphenylsulfide resins, polyphenyl sulfones, polyimide resins and mixtures thereof. The most preferred resins are aromatic polycarbonates, blends of aromatic polycarbonates and ABS, blends of polyphenylene ethers and high impact polystyrenes, and polyether imides.

[0014] The amount of phosphate employed can be that amount of phosphate which renders the thermoplastic molding resin composition flame retardant while maintaining good properties of heat deflection temperature, impact resistance and flow. Preferable the composition of the invention contains 3 to 25 weight percent of the phosphate flame retardant based on the total weight of thermoplastic resin and phosphate flame retardant and preferably 5 to 20 weight percent thereof.

[0015] The flame retardant of this invention is a combination of a low molecular weight and a high molecular weight phosphate. The flame retardant consists essentially of 10 to 90 weight % of the low molecular weight phosphate and correspondingly 90 to 10 weight % of the high molecular weight phosphate based on the weight of the flame retardant. Preferable the combination of phosphates consists essentially of 40 to 70 weight % of the low molecular weight phosphate and correspondingly 60 to 30 weight % of the high molecular weight phosphate. In addition, other additives may be employed with the composition of this invention such as other flame retardant enhancing additives, reinforcing additives such as glass fibers, other mineral additives such as mica, talc, oxides, including plasticizers, light and heat stabilizer, processing aides, impact modifiers, mold release agents, etc.

[0016] The compositions of this invention produce molded articles having a combination of excellent properties, depending on the thermoplastic resin employed and the application for the molded article. Preferably, molded articles from the composition of this invention have a matched Izod of at least about 266.5 J/m (5.0 ft.-lbs/in.), as determined in accordance with ASTM D 256, a heat deflection temperature under load of at least about 93°C (200°F) as determined in accordance with ASTM D 648, a flow of at least about 0.46 m (18") by the spiral flow measurement of a 3.18 mm (1/8") thick channel and a flammability rating of at least V1 as determined in accordance with Underwriters Laboratory Bulletin UL 94. IN the case of an ABS injection molding resin employing the flame retardant of this invention, an injection molded article may preferably have a notched Izod of at least about 373 J/m (7.0 ft.-lbs/in.), a heat deflection temperature under load of at least about 93°C (200°F), a flow of at least about 0.64 m (25.0") and a UL 94 rating of at least V1. In the case of a polyphenylene ether resin system employing the flame retardant of this invention, an injection molded article may preferably have a heat deflection temperature of at least about 93°C (200°F), a flow of at least about 0.38 m (15") and a UL 94 rating of at least V1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] The following Examples are provided to illustrate various embodiments of this invention. The Examples are for the purpose of illustration only, and should not be regarded as limiting the invention to any of the specific materials or conditions described therein.

EXAMPLE 1

[0018] The materials employed in this Example as components parts were as follows:

EP 0 747 424 B1

- PC- an aromatic polycarbonate derived from bisphenol-A and a carbonyl chloride (phosgene) having a weight average molecular weight of about 22,000 and an intrinsic viscosity (I.V.) of about 0.40 dI/g as measured in methylene chloride at 25°C
- HRG- a high rubber graft copolymer prepared by grafting a styrene-acrylonitrile onto a butadiene rubber in a 50/50 ratio
- Phosphate 1 - a mixture of several oligomeric diphosphates based on resorcinol
- Phosphate 2 - Bisphenol-A tetraphenyl diphosphate having a molecular weight of about 693.
- Phosphate 3 - Bisphenol-A phenyl polyphosphate having a molecular weight of about 10,056.
- PTFE - polytetrafluoroethylene

[0019] The components of the formulations as reported in Table 1 were compounded in a 30mm Werner Pfeider twin screw extruder at melt temperatures of about 288-293°C (550 - 560°F) and extruded. The extrudate was pelletized and the pellets were then dried at about 88°C (190°F) for about three (3) hours. The pellets were then molded into standard test specimens in accordance with the ASTM test procedure employed for determining the particular properties which are reported in Table 1 below. Impact resistance was determined by the Notched Izod impact test procedure ASTM D256 on molded specimens having a thickness of about 3.18 mm (1/8"). Heat deflection temperatures (HDT) under load 1820 KPa (264 psi) were measured on molded 6.35 mm (1/4") test bars in accordance with ASTM test procedure D648. Spiral flow measurements were performed in a 3.18 mm (1/8") thick channel at a melt temperature of about 249°C (480°F) and a mold temperature of about 66°C (150°F). The higher the length of the flow, the better is the flow of the specimen and easier to process. Flammability was determined on 15.9 mm (1/16") thick test specimens in accordance with Underwriters Laboratory Bulletin UL94 flammability rating V0, V1 and V2.

[0020] The results of the test are regarded in Table 1 below:

Table 1

Blend	1	2	3	4
HRG	81.05	80.05	80.05	80.05
Phosphate 1				11
Phosphate 2	10		6	
Phosphate 3		11	5	
PTFE	.2	.2	.2	.2
Additives	.95	.95	.95	.95
PROPERTIES				
Notched Izod (ft-lb/in)	9.0	7.1	8.6	2.3
HDT (°F)	204	236	214	188
Flow Channell (") m	(28) 0.71	(25.5) 0.65	(29.75) 0.76	(32.5) 0.83
UL 94 (1/16") 15.9 mm	V0	V2	V0	V0
Additives - stabilizer package of a hindered phenol, a phosphite and a lubricant				

EXAMPLE 2

[0021] Example 1 was repeated except that the formulations employed herein are as reported in Table 2 below. The polyphenylene ether employed had an I.V. of about 0.46 dI/g and was produced by General Electric Company. The high impact polystyrene (HPS) was produced by GE-Huntsman Co., Selkirk, New York, and had a weight average molecular weight of about 200,000 and a rubber content of about 10½ weight % based on the weight of the high impact polystyrene. The properties obtained were determined employing the same test procedures employed in Example 1. The results obtained are set forth in Table 2 below.

Table 2

Blend	1	2
Polyphenylene ether	50.5	50.5
High impact PS (HPS)	28	28
Phosphate 1	16.7	10.7
Phosphate 3	0	6.0
Polyethylene	1.25	1.25
Additives	1.0	1.0
Impact modifier	2.55	2.55
PROPERTIES		
HDT (°F) °C	(193) 89	(228) 109
Flow Channel (") m	(20.5) 0.52	(19.75) 0.50
UL 94	V0	V0
PS - Polystyrene Impact modifier - a styrene-butadiene block copolymer produced by Shell Chemical Co., Kraton G1650 Additives - a stabilizer package of a phosphite, an oxide and a sulfide Polyethylene - a mold release agent		

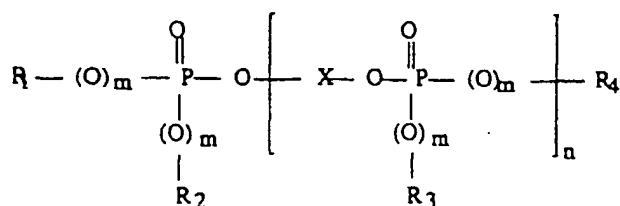
[0022] As shown from the Examples, the use of a low molecular weight and a high molecular weight phosphate produced results of good impact resistance, high heat deflection temperature under load, good flow for easy processing and excellent flame resistance. This is shown in Table 1 blend 3 in comparison to the other blends. Please note blend 1 which employed a low molecular weight bisphenol-A tetraphenyl diphosphate (oligomeric diphosphate); blend 2 which employed a high molecular weight bisphenol-A polyphosphate; and blend 4 which employed a mixture of oligomeric diphosphates. The unexpected results showed that the composition of this invention (blend 3) had good overall properties compared to the comparative blends 1, 2 and 4. In Table 2, equivalent results were obtained when employing a polyphenylene ether composition. Significantly better heat deflection temperature under load (1820 KPa) (264 psi) was obtained with the composition of this invention namely blend 2 of Table 2. Also flame retardant migration (juicing) was noticeably lacking from the composition of this invention.

[0023] In addition to the polymers employed in these Examples, the other polymers disclosed herein will produce equivalent results to those obtained with the polymers of Example 1 and 2.

[0024] While variations of this invention will be suggested to those skilled in the art, in view of the above disclosure, any such variations are intended to be within the scope of the claims appended hereto.

Claims

1. A moldable flame retardant thermoplastic resin composition comprising in admixture a moldable thermoplastic resin and a sufficient amount of a flame retardant to render the composition flame retardant, which flame retardant consists of, in combination, 10-90 weight % of a low molecular weight aromatic phosphate ester having a molecular weight of at least about 500 and from 90 to 10 weight % of a high molecular weight aromatic phosphate ester having a molecular weight of at least about 2300, providing that the molecular weights do not overlap each other, wherein the low molecular weight aromatic phosphate ester and high molecular weight phosphate ester are of the following formula:

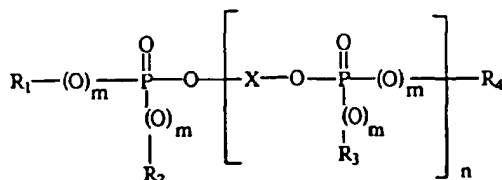


wherein R_1 , R_2 , R_3 and R_4 are independently selected from the group consisting of an aryl or an alkaryl group; X is derived from bisphenol-A; m is 0 or 1; n of said low molecular weight aromatic phosphate ester is an integer of from 1 to 5; and of said high molecular weight aromatic phosphate ester is an integer of from 6 to 35.

2. The composition of claim 1 wherein the low molecular weight phosphate has a molecular weight of 500 to 2000.
3. The composition of claim 1 wherein the high molecular weight phosphate has a molecular weight of 2300 to 11,000.
4. The composition of claim 1 wherein the thermoplastic resin is selected from the group consisting of aromatic polycarbonates, polyphenylene ethers, polyalkylene terephthalates, polyetherimides, polyetherimide esters, polyamides, styrene containing polymers and blends thereof.
5. The composition of claim 4 wherein the thermoplastic resin is an admixture of an aromatic polycarbonate and a styrene containing polymer.
6. the composition of claim 4 wherein the thermoplastic resin is an admixture of a polyphenylene ether resin and a high impact polystyrene.
7. The composition of claim 1 consisting essentially of 75 to 97 weight % of the thermoplastic resin and, correspondingly, 25 to 3 weight % of the flame retardant.

Patentansprüche

1. Formbare, flammhemmende thermoplastische Harzzusammensetzung, umfassend im Gemisch ein formbares thermoplastisches Harz und eine genügende Menge eines Entflammungshemmers, um die Zusammensetzung entflammungshemmend zu machen, wobei der Entflammungshemmer in Kombination aus 10-90 Gew.-% eines ein geringes Molekulargewicht aufweisenden aromatischen Phosphatesters mit einem Molekulargewicht von mindestens etwa 500 und 90-10 Gew.-% eines ein hohes Molekulargewicht aufweisenden aromatischen Phosphatesters mit einem Molekulargewicht von mindestens etwa 2.300 besteht, unter der Bedingung, dass sich die Molekulargewichte nicht überlappen, worin der ein geringes Molekulargewicht aufweisende aromatische Phosphatester und der ein hohes Molekulargewicht aufweisende Phosphatester die folgende Formel haben:

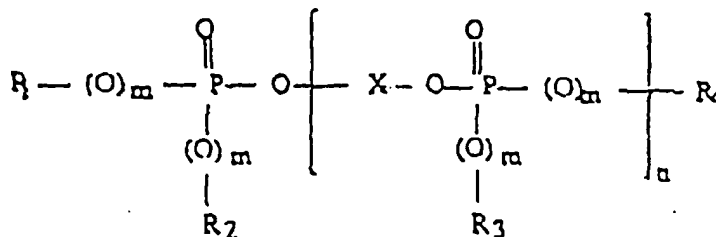


worin R_1 , R_2 , R_3 und R_4 unabhängig ausgewählt sind aus der Gruppe bestehend aus einer Aryl- oder einer Alkarylgruppe, X von Bisphenol-A abgeleitet ist, m 0 oder 1 ist, n des ein geringes Molekulargewicht aufweisenden aromatischen Phosphatesters eine ganze Zahl von 1 bis 5 und des ein hohes Molekulargewicht aufweisenden aromatischen Phosphatesters eine ganze Zahl von 6 bis 35 ist.

2. Zusammensetzung nach Anspruch 1, worin das ein geringes Molekulargewicht aufweisende Phosphat ein Molekulargewicht von 500 bis 2.000 hat.
3. Zusammensetzung nach Anspruch 1, worin das ein hohes Molekulargewicht aufweisende Phosphat ein Molekulargewicht von 2.300 bis 11.000 hat.
4. Zusammensetzung nach Anspruch 1, worin das thermoplastische Harz ausgewählt ist aus der Gruppe bestehend aus aromatischen Polycarbonaten, Polyphenylenethern, Polyalkylenterephthalaten, Polyetherimiden, Polyetherimidestern, Polyamiden, styrolhaltigen Polymeren und deren Mischungen.
5. Zusammensetzung nach Anspruch 4, worin das thermoplastische Harz ein Gemisch eines aromatischen Polycarbonats und eines styrolhaltigen Polymers ist.
6. Zusammensetzung nach Anspruch 4, worin das thermoplastische Harz ein Gemisch eines Polyphenylenetherharzes und eines schlagfesten Polystyrols ist.
7. Zusammensetzung nach Anspruch 1, bestehend im Wesentlichen aus 75 bis 97 Gew.-% des thermoplastischen Harzes und entsprechend 25 bis 3 Gew.-% des Entflammungshemmers.

Revendications

1. Composition moulable à base de résine thermoplastique, à inflammation freinée, qui comprend en mélange une résine thermoplastique moulable et une quantité d'un agent ignifugeant suffisante pour freiner l'inflammation de la composition, ledit agent ignifugeant étant constitué d'une combinaison de 10 à 90 % en poids d'un ester phosphate aromatique de faible masse moléculaire, ayant une masse moléculaire d'au moins environ 500, et de 90 à 10 % en poids d'un ester phosphate aromatique de masse moléculaire élevée, ayant une masse moléculaire d'au moins environ 2300, étant entendu que les masses moléculaires ne se chevauchent pas, l'ester phosphate aromatique de faible masse moléculaire et l'ester phosphate aromatique de masse moléculaire élevée répondant à la formule suivante :



dans laquelle R_1 , R_2 , R_3 et R_4 représentent chacun indépendamment un groupe aryle ou alkylaryle, X désigne le radical issu du bisphenol-A, m est égal à 0 ou 1, n désigne un nombre entier de 1 à 5 pour ledit ester phosphate aromatique de faible masse moléculaire, et un nombre entier de 6 à 35 pour ledit ester phosphate aromatique de masse moléculaire élevée.

2. Composition selon la revendication 1, dans laquelle le phosphate de masse moléculaire faible est un phosphate ayant une masse moléculaire de 500 à 2000.
3. Composition selon la revendication 1, dans laquelle le phosphate de masse moléculaire élevée est un phosphate ayant une masse moléculaire de 2300 à 11 000.
4. Composition selon la revendication 1, dans laquelle la résine thermoplastique est une résine choisie parmi les polycarbonates aromatiques, les poly(oxyde de phénylène), les poly(téréphthalates d'alkylène), les polyétherimides, les polyétherimideesters, les polyamides, les polymères contenant du styrène et leurs mélanges.
5. Composition selon la revendication 4, dans laquelle la résine thermoplastique est un mélange d'un polycarbonate

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aromatique et d'un polymère contenant du styrène.

6. Composition selon la revendication 4, dans laquelle la résine thermoplastique est un mélange d'une résine de poly (oxyde de phénylène) et d'un polystyrène à résistance aux chocs élevée.

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7. Composition selon la revendication 1, qui est constituée essentiellement de 75 à 97 % en poids de la résine thermoplastique et donc de 25 à 3 % en poids de l'agent ignifugeant.

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